



Short communication

Causal tree analysis of depth degradation of the lead acid battery

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H I G H L I G H T S

- ▶ Study the degradation analysis using fault tree and causal tree.
- ▶ Study the undesirable aging process of the battery during operation.
- ▶ Study the undesirable aging process of the battery during manufacturing process.
- ▶ Parameters variation of lead acid battery allows determining the degree of degradation.
- ▶ Judge the state of the battery lifetime.

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This paper aims to study the undesirable aging process or malfunctions state of the lead acid batteries using the fault and causal tree analysis during lead acid battery operation and during manufacturing process. The causal tree analysis presents the various possible combinations of events that involve the stratification of the electrolyte, the sulfating of the electrodes and the adherence loss of active mass to the grid. The parameters of electrical model are identified in order to found the degree of battery's degradation. The experimental determination of the variation interval of the parameters is done according to each of degradation mode. These modes are used in a diagnosis system allowing the identification of the depth of each aging process of the lead acid battery.

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1. Introduction

The emergence of new technologies in the electrical elements of storage made it possible to improve mass energies considerably. In spite of this spectacular progress, the use of these elements in the industrial applications remains problematic because of their lifetime. The main objective of this paper is to study the reliability of the lead acid battery by using analysis tools such as the causal tree and fault tree analysis. These tools [1,2] offer an undeniable framework for the inductive and deductive analysis in the industrial applications.

The reliability analysis of the lead acid battery is based on three stages.

The first stage consists of constructing a causal tree that presents the various possible combinations of events that involves the

batteries degradation during lead acid battery operation [3]. This degradation is generated by different physicochemical phenomena such as corrosion, sulfating, stratification and the non cohesion of active mass. In this paper the causal tree is extended to present the different fault during the manufacturing process.

The second stage consists of completing the causality chain by fault tree analysis (FTA) established using the basic elements of battery equivalent electrical circuit. Then for each aging mode, an experimental determination of the limit values of the circuit parameters is established.

The third stage consists of identifying the degradation modes of the lead acid battery with the experimental Nyquist diagram.

2. Degradation analysis using causal tree of the lead acid battery

The proposed causal tree of a lead acid battery is described in Fig. 1. The causal tree is a powerful technique that shows the causes

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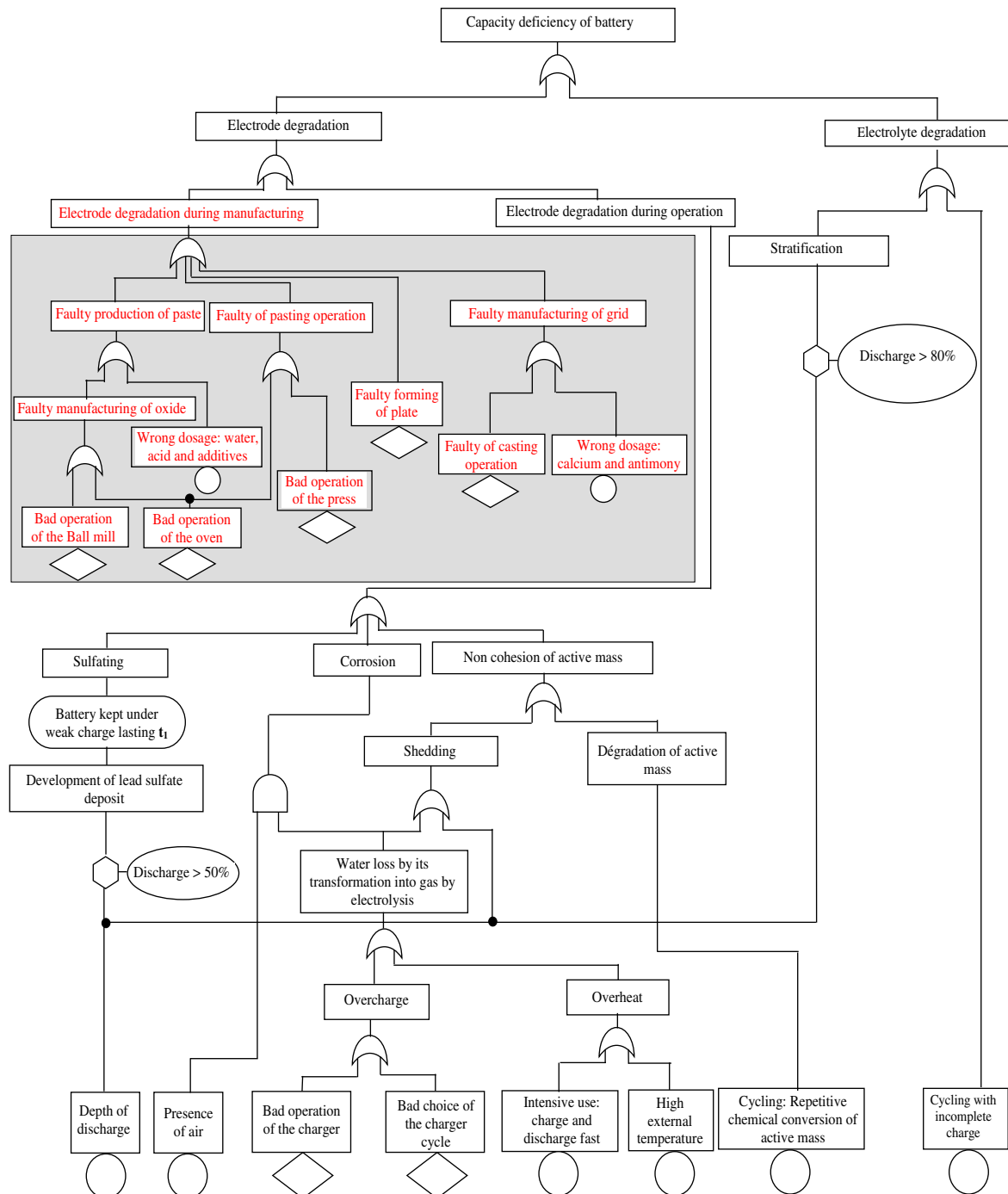


Fig. 1. Causal tree of lead acid battery.

of undesirable events in battery failure and presents all possible combinations of causes and faults leading to the loss of batteries capacity. The aging mechanisms of batteries are the actual chemical or mechanical events that generate battery's degradation. The battery can be affected in different ways depending on the conditions for which it is operated. All the types of lead acid batteries suffer from the same damage mechanisms but with different degrees. The major aging processes, leading to gradual loss of performance and eventually to the end of service life, are stratification of electrolyte, sulfating of the electrodes, corrosion of the electrodes and the loss of active mass adherence to the grid [4–6].

The deficiency of battery capacity can be caused in the manufacturing process of lead acid battery. This deficiency is accompanied by the failure of oxide manufacture, grid manufacture, paste production and pasting operation.

Lead oxide is manufactured from pigs of lead, is used to create the paste and is either produced by the Ball Mill or the Barton-like process. The chemical nature of the lead sulfate in the paste is important since it affects the facility with which the plate can be formed.

Grids are produced mainly by casting, pigs of hard lead are melted and molten is pour then cooled, trimmed, inspected, and stacked. The grids are then transported to the pasting.

The paste manufacturing process is very important as battery performance and life are determined by the properties of the paste. The paste and grids are later combined in the pasting process. Battery paste is made by mixing the oxide with water, acid and a range of proprietary additives. The paste is pressed by machine or hand into the grid lattice, and the plates are usually flash-dried in a high temperature oven.

Battery plates undergo an electrical formation process. In tank formation, plates are loaded into large baths of dilute acid and a direct current is passed to from the positive and negative plates. After drying, the plates are cut and assembly.

2.1. Stratification

The battery tends to be stratified if it is kept under weak charge and if it does not receive a complete charge. As the battery undergoes charge and discharge cycles, the distribution of electrolyte concentration becomes not uniform; the ions being heavier than water tend to accumulate at the bottom of the battery thus creating a stratification of electrolyte. Stratification leads to reduced battery capacity by concentrating the chemical reaction to specific parts of the electrodes.

2.2. Electrode sulfating

In the fundamental chemical reaction of the battery, sulfate crystals are created at both electrodes when the battery is discharged. In the charge cycle, the crystals dissolve and are converted to PbO_2 and Pb on respectively the positive and negative electrodes. However, if the battery is not operated properly, for instance if it is left at a low state of charge for a long period of time, the sulfate crystals grow in size and large sulfate crystals are created (Irreversible formation of lead sulfate in the active mass). Since these, large crystals do not dissolve easily when the battery is charged. This leads to hard or irreversible sulfating.

The consequence of sulfating is the creation of an insulating electrical layer that slows down the diffusion of the acid. Therefore, it is recommended to not discharge the battery more than 50% and regularly recharge the battery at 100%.

2.3. Electrode corrosion

The electrode corrosion has an impact on both the internal resistance and the available capacity. It is caused by the phenomenon of dehydration and it appears when the level of electrolyte is too low. The electrodes enter in contact with the air and oxidize [7]. The evaporation of electrolyte by its transformation into gas by electrolysis can come from an intensive use, a high external temperature and a high charging voltage.

2.4. Non cohesion of active mass

The non cohesion of the active mass is created by the active mass degradation and shedding. Over time, the active mass on the battery plates degrades and changes structure, loosing some of the electrical transfer properties and reducing the battery capacity [8]. The shedding is a process where the active mass of the plates falls down and collects at the bottom of the battery. It can eventually cause electrical short between positive and negative electrodes.

The shedding can be caused by overcharging the battery. The responsible mechanisms for the non cohesion of active mass are the depth of discharge and the repetitive chemical transformation (cycle of charge and discharge).

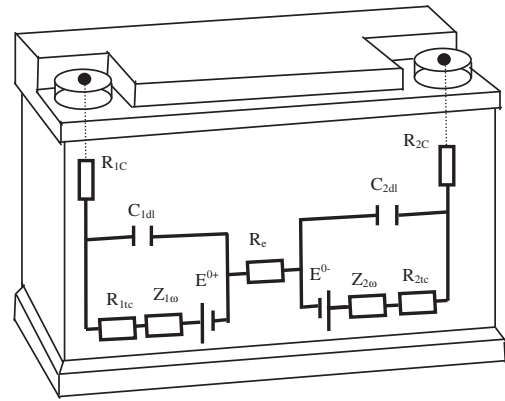


Fig. 2. Electrical equivalent circuit representing the electrochemical phenomena.

3. Degradation analysis using fault tree of the lead acid battery

The causality chain presented previously is supplemented by a fault tree analysis established using the basic elements of the equivalent electrical circuit of the battery. It is thus necessary to know which parameters will influence the starting of the degradation modes (stratification, sulfating, corrosion and the non cohesion of the active mass).

3.1. Electrical equivalent circuit of the battery

At the charge or discharge times of the battery, two great electrochemical phenomena act simultaneously on each electrode: static and dynamic phenomena [9–11]. As shown in Fig. 2, these phenomena are modeled by an electrical equivalent circuit.

To build the fault tree analysis, authors analyze the influence of each degradation mode on the variation of the elements of the electrical equivalent circuit.

The equilibrium potential of each electrode can be summed in a single term denoted by E_{eq} . This potential E_{eq} is measured at standard condition; it depends on the used electrolyte, which determines how many electrons will be released during the metal dissolution. The total potential of the battery is then the difference between the potentials of the two electrodes:

$$E_{eq} = E^{0+} - E^{0-} \quad (1)$$

The internal resistance of the battery results in the sum of two distinct terms. The first term is the various connector resistances R_{1C} and R_{2C} , the second term is the resistance of the electrolyte R_e .

$$R_Q = R_{1C} + R_{2C} + R_e \quad (2)$$

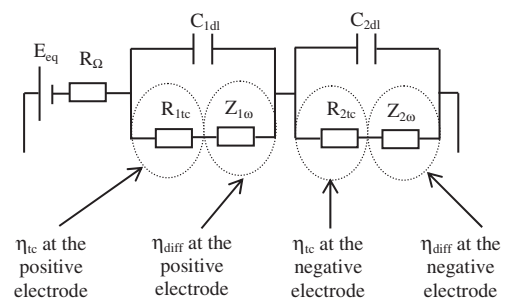


Fig. 3. Electrical equivalent circuit showing over voltage to the levels of the electrodes.

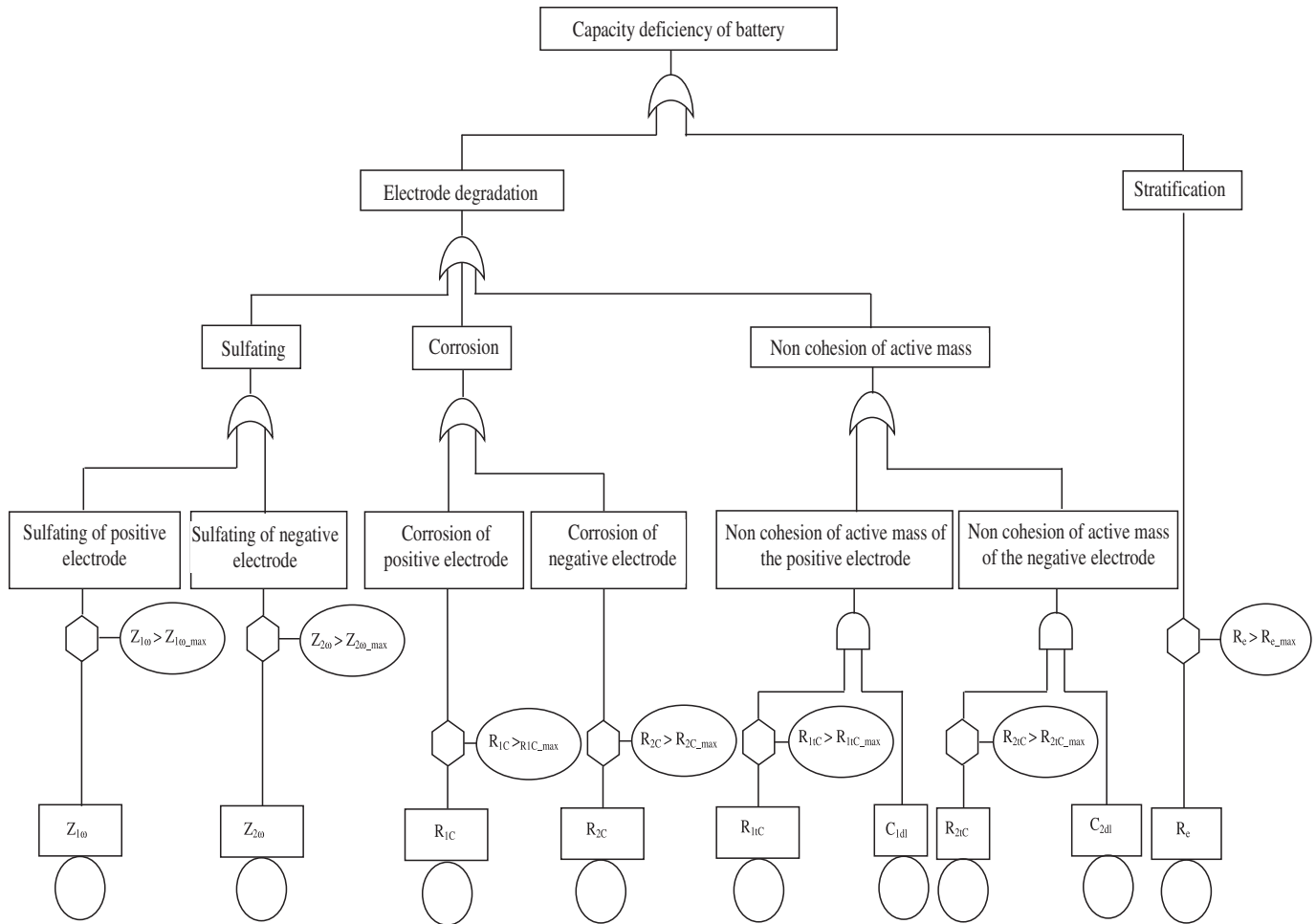


Fig. 4. Fault tree of lead acid battery.

The variation of this resistance shows the existence of the stratification phenomenon, the corrosion and the mechanical deterioration of the electrodes.

C_{1dl} and C_{2dl} represent the double layer capacitance on each electrode. The double layer capacitance is the capacitance caused by a charge distribution between the electrode and the electrolyte.

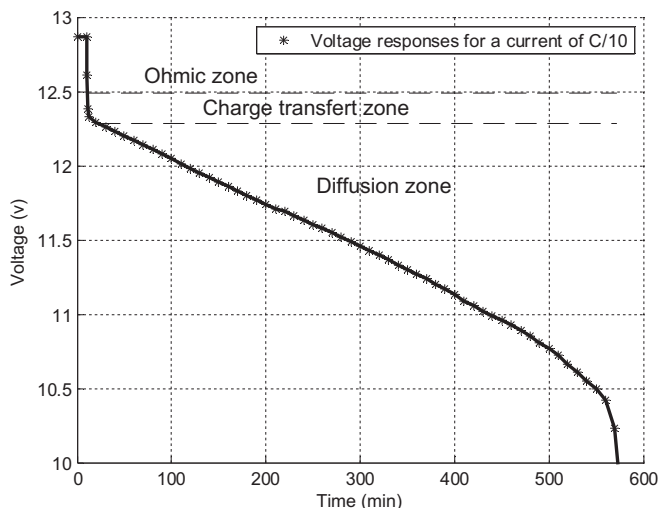


Fig. 5. Voltage response of the battery during the phase of discharge.

R_{1tc} and R_{2tc} represent the phenomenon of charge transfer between the electrode and the electrolyte which causes on the electrode potential an over voltage of charge transfer η_{tc} . Their variation during the cycle life of battery generates a η_{tc} and shows the non cohesion of the active mass.

$Z_{1\omega}$ and $Z_{2\omega}$ represent the phenomenon of diffusion. The diffusion layer is caused by the grade of concentration of the electrolyte near the electrode, which causes on the electrode potential a second over voltage called “over voltage of concentration” η_{diff} . This effective impedance is also called the Warburg impedance. Their variation during the cycle life of battery generates a η_{diff} and indicates that the battery is sulfated.

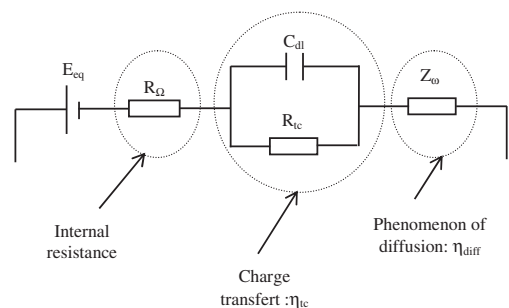


Fig. 6. Electrical equivalent circuit simplified for the identification of parameters.

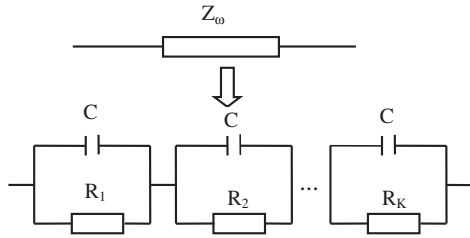


Fig. 7. Warburg impedance.

The electrical circuit considered is represented in the following (Fig. 3).

The parameters of electrical equivalent circuit vary during the life cycle of the battery. These variations involve an increase in the internal impedance and a rise in the voltage drop of charge transfer and of diffusion. Fig. 4 presents all these variations and their effects on degradation of the battery.

3.2. Parameters identification of the electrical equivalent circuit

The parameters identification of the electrical equivalent circuit is carried out with experimental measurements on a lead acid battery of Tunisian mark ASSAD SOLAR SLP 110 having a capacity of 110 AH. This battery is used in rural electrification, isolated sites, photovoltaic, pumping irrigation, telecommunications etc.

The measurement of the terminal voltage of the battery following a discharge with a constant current of $C/10$ is given in Fig. 5.

The plan of the voltage response enables to graphically visualize three influence zones: the internal resistance, the charge transfer and the diffusion phenomenon. That leads to dissociate the electrical structure in three distinct electrical elements. Thus, the final electrical circuit used for the identification of the battery's parameters is given in the following (Fig. 6).

The impedance's expression of the equivalent circuit is:

$$Z_T = R_\Omega + \frac{R_{tc}}{1 + R_{tc}C_{dl}(j\omega)} + Z_\omega \quad (3)$$

The physical interpretation of diffusive phenomenon [11] is modeled as:

$$Z_\omega(s) = \left(\frac{K_2}{\sqrt{s}} \tanh \left(\frac{K_1}{K_2} \sqrt{s} \right) \right) = \left(\frac{K_1}{\sqrt{s} \cdot \tau_d} \tanh(\sqrt{s} \cdot \tau_d) \right) \quad (4)$$

The calculation of inverse Laplace transform reveals an infinite sum of parallel RC cells (Fig. 7).

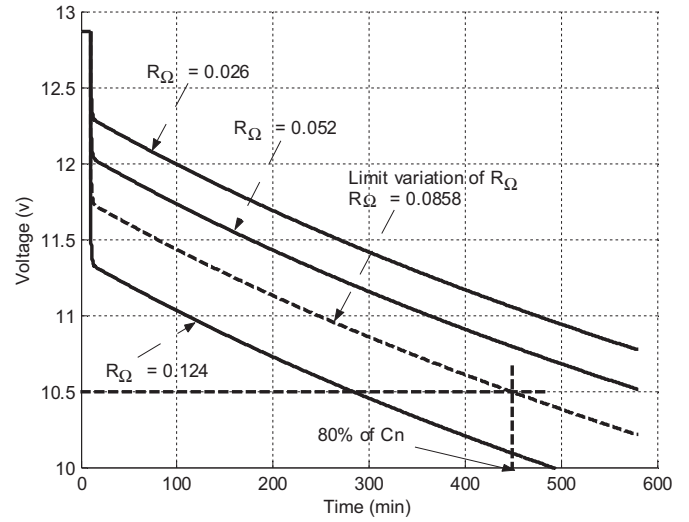
The expressions of the constants are identified by the following system:

$$C_\omega = \frac{K_1}{2K_2^2}, \quad R_{\omega,k} = \frac{8 \cdot K_1}{(2k-1)^2 \pi^2} \quad (5)$$

Note that through the observation of Fig. 5 that the voltage response presents a voltage drop in discharge at the potential of the

Table 1
Estimated parameters of the electrical circuit.

E_{eq} (V)	12.8
R_Ω (Ω)	0.026
R_{tc} (Ω)	0.031
C_{dl} (F)	33
K_1	9
K_2	$9 \cdot 10^{-3}$

Fig. 8. Limit variation of R_Ω .

electrode. This voltage drop represents the sum of voltage drop of Ohmic, activation and diffusion.

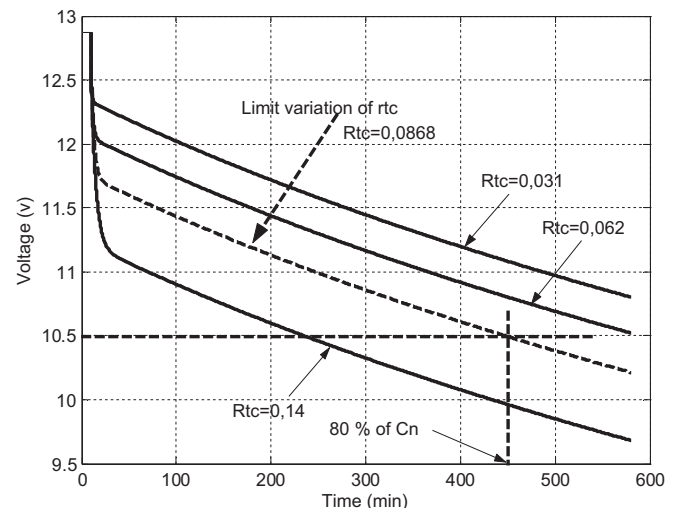
$$V_{Bat} = E_{eq} - \eta_{Ohmic} - \eta_{tc} - \eta_{diff} \quad (6)$$

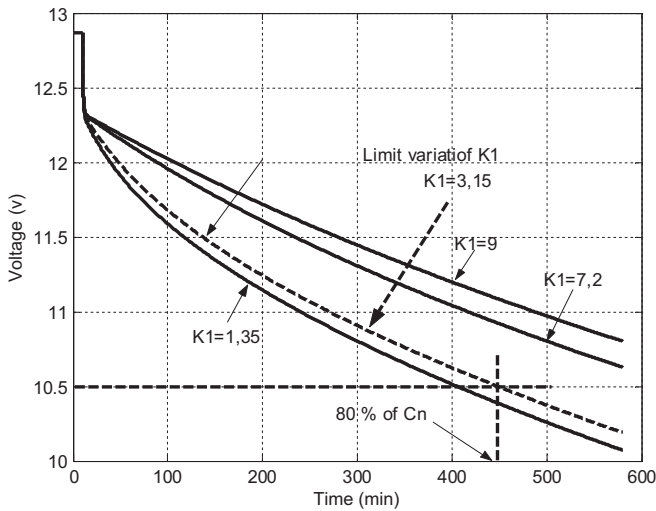
These voltage drops allow identifying the parameters of the electrical equivalent circuit (Table 1).

3.3. Interval of parameters variation of the electrical equivalent circuit simplified

The lifetime of a battery is achieved when its potential capacity falls to 80% from its nominal capacity. Figs. 8–11 present the limits of the parameters of the electrical circuit for which it is admitted that the battery is degraded. These limits are given for a voltage at the end of the discharge of 10.5 V with a potential capacity of 80% of C_n .

The parameters variation intervals of the electrical equivalent circuit are given in Table 2.

Fig. 9. Limit variation of R_{tc} .

Fig. 10. Limit variation of K_1 .

3.4. Simplified fault tree analysis

Fig. 12 presents the parameters variations of the simplified electrical circuit and their effects on batteries degradation.

The Warburg time constant τ_d (Eq. (4)) represents the ratio of the effective coefficient diffusion D over the square of the effective diffusion thickness as:

$$\tau_d = \left(\frac{K_1}{K_2} \right)^2 = \frac{\delta^2}{D} \quad (7)$$

δ : Nernst diffusion layer thickness.

D : an average value of the diffusion coefficient.

The crystallization process during sulfating: modified morphology of electrodes, reduced porosity electrodes and decreased consequently the thickness of Ernest diffusion layer. The thickness of the Nernst diffusion layer varies within the range 0.1–0.001 mm.

In batteries, the charge transfer coefficient is the parameter that signifies the fraction of over potential that affects the current density. This transfer coefficient is the heart of electrode kinetics.

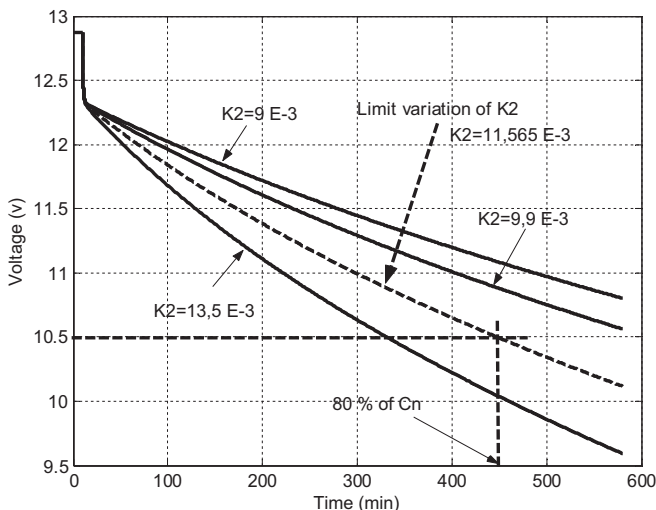
Fig. 11. Limit variation of K_2 .

Table 2
Intervals of parameters variation.

Parameters of electrical circuit	Values for new battery	Limiting values	Interval of maximum variation
Internal resistance: R_0	0.026 Ω	0.0858 Ω	$\Delta R_{0\max} = 0.0598 \Omega$
Charge transfer resistance: R_{tc}	0.031 Ω	0.0868 Ω	$\Delta R_{tc\max} = 0.0558 \Omega$
Warburg impedance: K_1	9	3.15	$\Delta K_{1\max} = 5.85$
Warburg impedance: K_2	9×10^{-3}	11.565×10^{-3}	$\Delta K_{2\max} = 2.565 \times 10^{-3}$

R_{tc} refers to the charge transfer resistance: that is, the losses due to ionization of lead. This parameter is associated with the exchange current I_0 of the electrochemical reaction of battery as follow:

$$R_{tc} = \frac{RT}{I_0 F} \quad (8)$$

R : molar gas constant.

T : temperature.

F : Faraday's constant.

The exchange current is proportional to the surface concentration of the species participating in the electrochemical reaction. Thus lower R_{tc} values correspond to higher Pb^{2+} local concentration at the lead surface [12].

The increase in charge-transfer resistance values is due to the conversion of both Pb and PbO_2 to poorly. If the charge transfer resistance is too high then the battery will never recharge.

The internal resistance R_0 increases as the corrosion layer increases because of the reduced conductivity of the corroded material and due to the reduced cross section of the grid.

4. Battery diagnosis

The diagnosis of used lead acid battery is thus carried out in accordance with the experimental protocol represented in Fig. 13.

As shown by Table 3, the parameters of the equivalent electrical circuit of the new battery in different states of charge are identifying with experimental measurements of the voltage response to a constant discharge current $C/10$. A database of parameters ranges in different SOC is achieved.

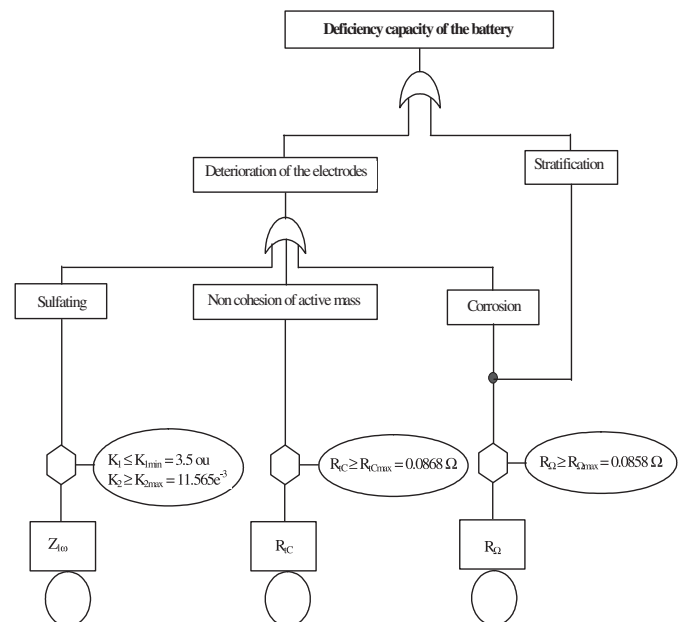


Fig. 12. Simplified degradation fault tree analysis of the deficiency capacity.

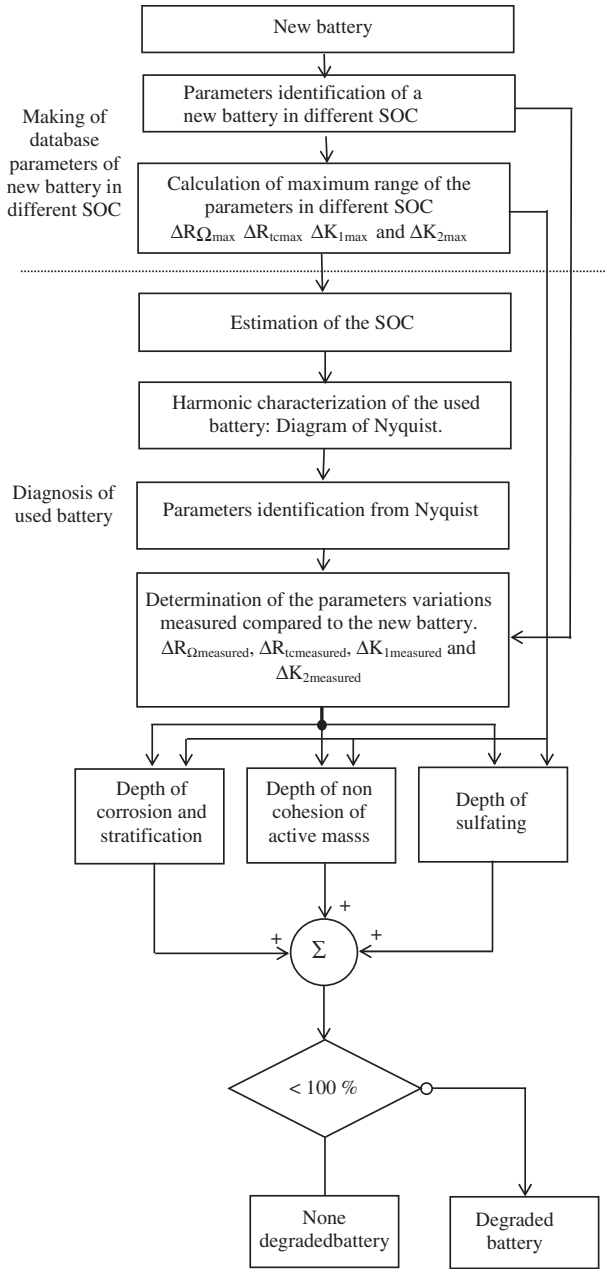


Fig. 13. Synoptic diagram of the diagnosis system.

The diagnosis of the tested battery starts with estimation of the SOC.

A battery is degraded by the superposition of the various degradation modes (sulfating, stratification, corrosion and non cohesion of active mass). Figs. 14–16 represent the experimental Nyquist diagram of 3 batteries (a new battery and 2 used batteries).

For each battery, a parametric identification of R_Ω , R_{tc} , K_1 and K_2 using Nyquist diagrams is carried out. Then the variations

Table 3
Parameters variation according to the state of charge.

State of charge	R_Ω (Ω)	R_{tc} (ω)	C_{dl} (F)	K_1	K_2
100%	0.026	0.031	33	9	9×10^{-3}
80%	0.030	0.033	30	8.9	9.2×10^{-3}
60%	0.033	0.036	26	8.6	9.8×10^{-3}
40%	0.037	0.041	22	8	11×10^{-3}

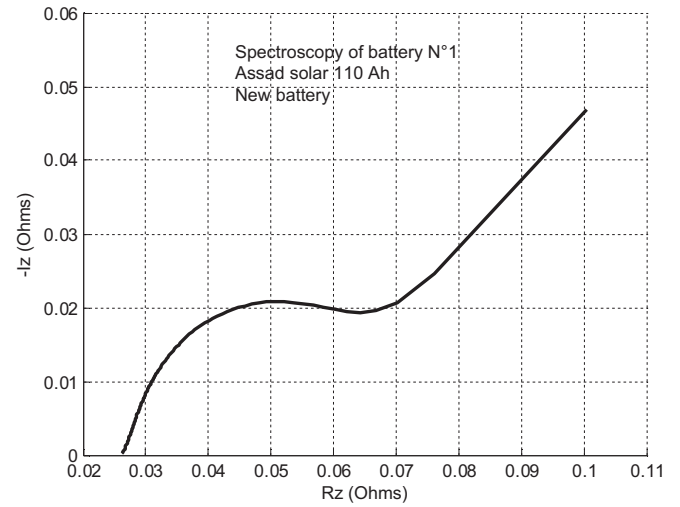


Fig. 14. Diagram of Nyquist of the battery tested No. 1. Fully charged.

$\Delta R_{\Omega\text{measured}}$, $\Delta R_{tc\text{measured}}$, $\Delta K_{1\text{measured}}$ and $\Delta K_{2\text{measured}}$ of a used battery are calculated and then compared to the variations parameters of a new battery.

The coefficients α_1 , α_2 , α_3 and α_4 present the depth of each degradation mode in percentage (Table 4).

The variable α_1 presents the depth of corrosion and stratification in percentage:

$$\alpha_1 = 100 \cdot \frac{\Delta R_{\Omega\text{measured}}}{\Delta R_{\Omega\text{max}}} \quad (9)$$

The variable α_2 presents the depth of non cohesion of active mass in percentage:

$$\alpha_2 = 100 \frac{\Delta R_{tc\text{ measured}}}{\Delta R_{tc\text{ max}}} \quad (10)$$

The sum of the variables α_3 and α_4 presents the depth of sulfating in percentage where:

$$\alpha_3 = 100 \frac{\Delta K_{1\text{measured}}}{\Delta K_{1\text{max}}} \quad (11)$$

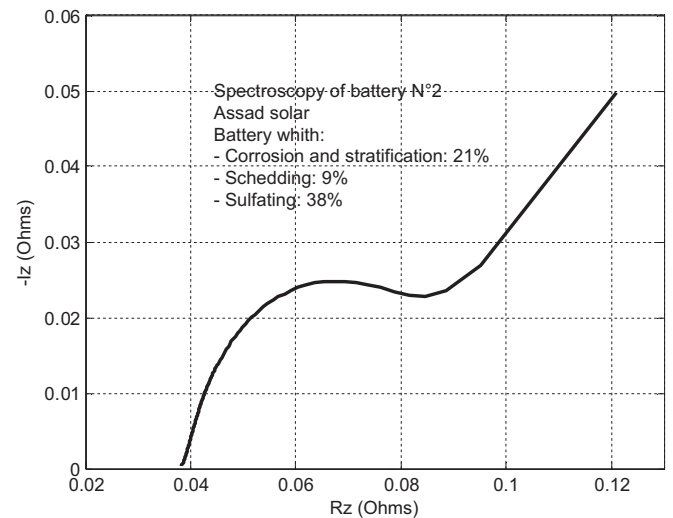


Fig. 15. Diagram of Nyquist of the battery tested No. 2. Fully charged.

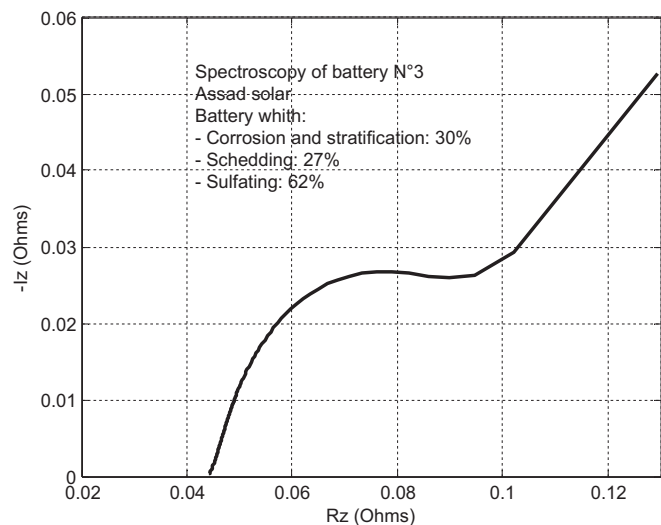


Fig. 16. Diagram of Nyquist of the battery tested No. 3. Fully charged.

Table 4
Different degree of each degradation mode.

	Battery No. 2	Battery No. 3
α_1	21%	30%
α_2	9%	27%
α_3	18%	24%
α_4	20%	38%
Parameter variation of %	68%	119%
Aging of battery	Non degraded	Degraded battery

$$\alpha_4 = 100 \frac{\Delta K_{2\text{measured}}}{\Delta K_{2\text{max}}} \tag{12}$$

We recall that the criterion of degradation is fixed at 80% of nominal capacity for a voltage at the end of discharge of 10.5 V.

The coefficients α_1 , α_2 , α_3 and α_4 show the losses of the battery capacity in %.

Indeed for a used battery the calculated from these coefficients allows to determine the loss of battery capacity in % for each degradation mode. A battery is degraded by the superposition of different degradation modes, thus the criterion of degradation is reached if the sum $\alpha_1 + \alpha_2 + \alpha_3 + \alpha_4$ equals 100%.

The sum $\alpha_1 + \alpha_2 + \alpha_3 + \alpha_4$ indicates the aging of battery, it is considered degraded if the sum exceeds 100%.

5. Conclusion

The paper presents an approach using analysis tools of reliability to describe the various phenomena causing the capacity deficiency of lead acid battery. This approach is based on a causal tree analysis to describe the origin of the capacity deficiency and a fault tree analysis to study the degradation through the examination of the parameters variation of the electrical equivalent model.

Finally, this parameters variation of lead acid battery allows to determine the degree of each degradation mode and to judge the state of this lifetime.

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